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(54) Title: ALGICIDAL AND FUNGICIDAL PRESERVATIVE WITH ALTERNARIA-ACTIVITY

(57) Abstract

The present application describes a preservative which comprises a) at least one compound from the class of the pyrithiones which are active against Alternaria and b) at least one compound from the class of the algicidally active triazines and/or c) at least one compound from the classes of the fungicidally active benzimidazoles or thiophenes and customary auxiliaries, where, in the absence of benzimidazole or thiophene, an additional presence of algicidal urea compounds or biocidal hydrolysable polymeric resins is excluded.

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Algicidal and fungicidal preservative with Alternaria-activity

The invention relates to preservatives for imparting biocidal properties to objects or coatings whose surfaces are, as experience shows, frequently attacked by algae or fungi. Furthermore it relates to a process for their preparation and to their use.

Attack by algae and fungi is not only optically unattractive, but subsequent growth of lichen or moss can lead to the material being damaged and the service life reduced. Microbial attack of objects or coatings applied thereto is particularly prevalent under conditions with high atmospheric humidity, for example under the conditions of the food industries, in dairies, breweries or on the north faces of buildings. Furthermore, discoloration as a result of UV light irradiation and the effect of heat is a frequently undesirable secondary effect. In particular coatings such as paints, varnishes, and renders are affected.

The attempt to solve the above-described problem by adding pulverulent additives to the coating materials used entails a large number of disadvantages upon use. Furthermore, the demand for solvent-free or low-solvent preparations resulted in the development of aqueous dispersions in which known fungicidal and algistatic or algicidal active ingredients which are insoluble in water were employed. A particular problem in this context is the fungicidal treatment of Alternaria species which occur frequently, despite the imparting of fungicidal and algistatic properties to, for example, coatings with commercially available products on coats of paint, varnish and render. Frequently, the efficacies of the commercially available dispersions differ greatly, some dispersions being known which have a fairly good fungicidal and algicidal activity, but which leave something to be desired with regard to discoloration when exposed to environmental factors such as light, temperature and

humidity. In addition, while such aqueous dispersions have good stability and resistance to leaching, their stability is frequently no better than poor.

DE 42 42 082 A1, for example, discloses polymeric binder systems for growth-inhibitory paint compositions for the protection of maritime surfaces which, in addition to biocidal hydrolysable polymeric resins and customary auxiliaries and additives, comprise dichlorophenyldimethylurea, 2-methylthio-tert-butylamino-6-cyclopropylamin-s-triazine, zinc pyrithione, 2-(thiocyanomethyl)benzothiazole, 4,5-dichloro-2-N-octyl-4-isothiazolin-3-one or 2,4,5,6-tetrachlorophthalonitrile or dichlorofluanid as co-biocide. In these systems, even the hydrolysable polymeric resins are biocidal and replace the organotin compounds previously used in antifouling paints which were due to be replaced for environmental reasons.

DE 44 33 856 A1 furthermore discloses an antifouling composition which comprises 2-mercaptopyridine-N-oxide and/or its metal complexes and also algicidal urea. In addition to these two components, additional antifouling agents may be added, such as, for example, 2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine.

DE 42 42 389 A1 furthermore discloses an aqueous dispersion with fungicidal and algicidal activity which comprises a combination of carbendazim, 2-thiocyanomethylthiobenzothiazole and 2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine. Even though the algicidal and fungicidal action of such a dispersion are good, the stability to discoloration leaves room for improvement. Also, the emissions of certain secondary components (of the benzothiazol) are disadvantageous since higher concentrations can lead to unpleasant odour.

There is furthermore the product Acticid EP from Thor Chemie, which contains diuron (1,1-dimethyl-3-(3,4-dichlorophenyl)urea) (an algicide) plus carbendazim (a fungicide) plus N-octylisothiazolone (an active ingredient against Alternaria). While this product has a comparably

good algicidal and fungicidal action, the activity against Alternaria is only unsatisfactory, in particular under stress due to leaching. Moreover, the diuron in Acticid EP is an organochlorine-containing algicide which is unacceptable from the ecotoxicological point of view.

Another product, Mergal S90 from Riedel de-Haen, contains an algicidal triazine derivative, fungicidal carbendazim and N-octylisothiazolone as active ingredient against Alternaria. However, the activity against Alternaria under stress due to leaching is insufficient.

In addition, the abovementioned compositions contain liquid organic active ingredients against Alternaria, whose incorporations into, for example, aqueous dispersions are technically complicated and make the manufacture of the products more expensive. They are insoluble in water, sparingly dispersible (with the use of additional auxiliaries which adversely affect resistance to leaching) and adversely affect the stability of the dispersion.

In addition, even when the known compositions with at least some degree of activity against Alternaria exhibit a sufficiently high algicidal and fungicidal activity, the stability to discoloration in particular is, as a rule, moderate to poor.

It is therefore an object of the invention to provide preservatives and in particular film preservatives with a fungicidal and algistatic activity, including a good activity against Alternaria species, and which, moreover, exhibit a good stability to discoloration.

This object is achieved by a preservative according to Claim 1, which is characterized in that it comprises

a) at least one compound from the class of the pyrithiones which are active against Alternaria and
b) at least one compound from the class of the algicidally active triazines and/or

c) at least one compound from the classes of the fungicidally active benzimidazoles or thiophenes

and customary auxiliaries and additives,

where, in the absence of benzimidazole or thiophene, the additional presence of algicidal urea compounds or biocidal hydrolysable polymeric resins is excluded.

Preferred embodiments are the subject-matter of the subclaims.

The preservative according to the invention is distinguished by its good microbiological activity against fungi (specifically Alternaria species) and algae. The biocidal action can also be achieved over a prolonged period under high stress due to leaching. The stability to discoloration is extremely good.

The preservatives according to the invention are distinguished, in toto, by the following characteristics:

- good algicidal action
- good fungicidal action
- good activity against Alternaria species or other problem microorganisms which are relatively difficult to inactivate in the field of preservation, in particular film preservation, or of the protection of materials (coatings, imparting of antifouling properties and the like)
- good action even when under stress due to leaching, UV stress, temperature stress or under extreme weather or climatic conditions or alternating weather conditions
- low in emission and odour
- no, or negligible interactions with the material to be protected or with constituents of coating materials used, when applied correctly, in particular no tendency to develop discolorations and the like

- no tendency to develop discolorations caused by environmental factors such as light, high temperatures, humidity and the like
- simple preparation of dispersions, in particular aqueous dispersions
- use of AOX-free additives and active ingredients (AOX = adsorbable organic halogen compounds)
- free from low-boiling organic solvents
- use of as little organic solvent as possible
- stability of the dispersion good to very good
- homogeneous mixtures with good flow properties
- no sediment formation upon storage
- low resistance of the active ingredients to hydrolysis
- long-term action combined with low use concentration
- low mammal toxicity
- advantageous price/performance ratio
- low vapour pressure of the active ingredients.

It is essential that the preservative according to the invention is a combination of a) at least one pyrithione which is active against Alternaria and b) at least one algicidally active triazine or c) a fungicidally active benzimidazole or thiophene. The scope of the invention also extends to combinations of compounds from in each case all three classes of active ingredients a), b) and c).

The preservative has a total active ingredient content, that is to say a content of a) and b) and/or c), if present, in a range from 1 to 99% by weight, preferably 2 to 90% by weight, in particular 5 to 80% by weight and more preferably 5 to 60% by weight or even up to 40% by weight, the remainder being composed of customary formulation auxiliaries and additives.

For example, the preservative comprises:

a) 1.0 to 45.0% by weight of pyrithione compound and

b) 1.0 to 35.0% by weight of triazine compound and/or

c) 1.0 to 45.0% by weight of benzimidazole or thiophene compound.

Preferably, the preservative comprises:

a) 2.0 to 25.0% by weight of pyrithione compound and
b) 2.0 to 15.0% by weight of triazine compound and/or
c) 2.0 to 25.0% by weight of benzimidazole or thiophene compound.

More preferably, the preservative comprises:

a) 2.0 to 15.0% by weight of pyrithione compound and
b) 2.0 to 10.0% by weight of triazine compound and/or
c) 2.0 to 15.0% by weight of benzimidazole or thiophene compound.

Especially suitable pyrithione compounds are the pyrithione salts, and zinc pyrithione is particularly preferred. Preferred triazine compounds are 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, N^2,N^4-diisopropyl-6-methylthio-1,3,5-triazine-2,4,-diamine and N^2-tert-butyl-N^4-ethyl-6-methylthio-1,3,5-triazine-2,4-diamine, with 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine being especially preferred. Preferred amongst the benzimidazole compounds is carbendazim, and preferred amongst the thiophene compounds is N-cyclohexyl-2-aminobenzothiophene S,S-dioxide.

Specifically preferred embodiments which comprise in each case one compound from amongst a), b) and c) contain 2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine, carbendazim and zinc pyrithione.

Another embodiment according to the invention comprises a combination of a) and b) and, more preferably, of 2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine and zinc pyrithione.

A further embodiment according to the invention which comprises a combination of a) and c) contains carbendazim and zinc pyrithione.

In addition to the two or three active ingredients a) and b) and/or c) which are necessarily present in accordance with the invention, it is also possible for one or more further algistatic and/or fungicidal active ingredients to be present. These are preferably halogen-free. They comprise, for example, thiabendazole, thiocyanomethylthiobenzothiazole (TCMTB), N-octylisothiazolone, iodopropinyl butylcarbamate (IPBC), diiodomethyl p-tolyl sulphone and isothiazolone Binte salts, for example of N-octylisothiazolone and benzisothiazolone. In each case, they may amount to up to 10% by weight, but in total they may not amount to more than 30% by weight.

In addition to the active ingredients, the preservative according to the invention can furthermore contain customary auxiliaries and additives such as dispersants, high-boiling solubilizers, anti-caking agents, thickeners, antifoams, low-temperature stabilizers, fillers and/or carriers.

Substances which are suitable as dispersants are, for example, non-ionic surfactants such as fatty alcohol ethoxylates. Also useful are salts of polyacrylic acid. Examples of particularly suitable substances are C_{10}-oxoalcohol having 3 ethyleneoxy groups, C_{13}-oxoalcohol having 3 or 5 ethyleneoxy groups, C_{12}-C_{14}-fatty alcohol having 2.5 ethyleneoxy groups and lauryl alcohol polyglycol ether having 3 ethyleneoxy groups. These dispersants can be employed in each case alone or as a mixture of one or more of these compounds. Preferred substances are non-ionic fatty alcohol ethoxylates having 2 to 9 ethyleneoxy groups. The dispersants can be employed in an amount of up to 30% by weight, in particular up to 10% by weight, and preferably up to 2% by weight, amounts of, for example, 0.7% by weight also being suitable.

Examples of high-boiling solubilizers are glycols, their esters or ethers such as ethylene glycol, diethylene glycol, polyethylene glycol (300 to 600 dalton) or their mono- or dialkyl ethers, propylene glycol, dipropylene

glycol, polypropylene glycol, their mono- or dialkyl ethers, butylene glycol, dibutylene glycol, their mono- or dialkyl ethers or the corresponding alkyl esters, the alkyl groups having in each case 1 to 10, and preferably 1 to 4, carbon atoms. Especially preferred are 1,3-butylene glycol and polyethylene glycol 400 (the average molecular weight is 400). Mixtures of these solubilizers may also be employed. In some cases, the solubilizers in the preservatives have a consistency-regulating (thickening or thinning) action and/or act as low-temperature stabilizers (antifreeze agents). The solubilizers can be employed in an amount of up to 15 % by weight, in particular up to 10 % by weight, and preferably up to 8 % by weight. Especially preferred amounts are 4 to 8 % by weight.

Preferred mixtures of dispersants and solubilizers comprise:

10 % by weight of	C_{13}-oxoalcohol having 5 ethyleneoxy groups
4-8 % by weight of	lauryl alkyl polyglycol ether having 3 ethyleneoxy groups (preferably 6 % by weight) and
4-8 % by weight of	butane-1,3-diol or of a mixture of butane-1,3-diol and polyethylene glycol 400 (preferably 6 % by weight) or
2-8 % by weight of	polyethylene glycol 400 (preferably not less than 4 % by weight).

A further preferred dispersant/solubilizer/thickener system comprises Rhodopol 50 MD + Lutensol TO 5. Rhodopol 50 MD is a suspension stabilizer and a structurally viscous thickener on a xanthan gum base (heteropolysaccharide) with a molecular weight of approx. 2 million g/mol. It is an anionic polymer which is soluble in cold and hot water. Lutensol TO 5 is a tridecyl alcohol ethoxylate with 5 EO. Rhodopol 50 MD is employed, for example, in an amount of 0.5 % by weight, while Lutensol TO

5 is employed, for example, in an amount of 0.5 % by weight, so that, for example, 0.7 % by weight of the dispersant/solubilizer/thickener system may be present in total.

In particular the stability and manageability of preservatives which contain such dispersants and/or solubilizers is surprisingly good even after prolonged storage and even under very unfavourable temperature and humidity conditions. As a rule, even separation of the mixture of preservative components is avoided.

The active ingredient combination according to the invention can exist in the form of a powder, a homogeneous liquid, for example a solution, a dispersion or a paste, it preferably being flowable.

The individual constituents of the preservative, that is to say the components of the preservative, preferably have a particle size of < 70 µm, preferably < 30 µm and in particular < 10 µm. Such a particle size can be obtained by superfine grinding of the solid active constituents. Grinding preferably takes place in the wet state using bead and/or ball and/or colloid mills.

The preservative according to the invention can be prepared by the customary processes known to those skilled in the art. For example, it is prepared by superfine grinding of the solid active constituents in water in the presence of the remaining formulation auxiliaries to give a premix and, if appropriate subsequently stirring the liquid active components into this premix. Thus, for example, the active constituents 2-methylthio-4-t-butyl-amino-6-cyclopropylamino-s-triazine, carbendazim and zinc pyrithione can first be subjected to wet superfine grinding, and a further active ingredient can subsequently be stirred in.

The preservative according to the invention can be used as a biocidal additive to coatings, to polymer dispersions, in particular those which are film-forming and are based on polyacrylate, for the treatment of

surfaces and materials, and for imparting fungicidal and algistatic properties to paints, varnishes and renders. It can also been used in textile finishing, sealants, glues and adhesives.

The efficacy of preservatives according to the invention can be seen from the following tests.

Film preservative with compounds from active ingredient classes a), b) and c)

Results from tests for determining the fungicidal/algicidal action:

Test material: Masonry paint

	% by weight
Texanol	1.20
Natrosol 250 HBR	0.30
Water	19.95
Calgon N, 10% in water	0.20
Pigment dispersant A	0.25
Antifoam Nopco 8034, 50% in water	0.12
Ammonia, 25%	0.50
Titanium dioxide Kronos RN56	20.00
Durcal 5	10.00
Millicarb	10.40
Aluminium silicate P 820	2.00
Plextol D 498	35.00
Antifoam Nopco 8034	0.08

Test type: Imparting fungicidal properties
Imparting algistatic properties

Test microorganisms, algae:	Chlorella fusca	CF
Test microorganisms, fungi:	Aspergillus niger	AN
	Penicillium funiculosum	PF
	Alternaria alternata	AL

Test substances:

Blank value Masonry paint, unpreserved

I) 19.9% 1,1-dimethyl-3-(3,4-dichlorophenyl)urea (diuron) + 8.1% carbendazim + 6.72% N-octylisothiazolone (Kathon 893; 46.1%); aqueous dispersion (corresponding to Acticid EP) (comparison dispersion)

II) 4.38% 2-methylthio-tert-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051) + 10.0% carbendazim + 7.0% N-octylisothiazolone (Kathon 893; 46.1%); aqueous dispersion (comparison dispersion)

III) 4.38% 2-methylthio-tert-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051) + 10.0% carbendazim + 5.0% diiodomethyl p-tolyl sulphone (Amical 48); aqueous dispersion (comparison dispersion)

IV) 4.38% 2-methylthio-tert-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051) + 10.0% carbendazim + 10.0% diiodomethyl p-tolyl sulphone (Amical 48); aqueous dispersion (comparison dispersion)

V) 4.38% 2-methylthio-tert-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051) + 10.0% carbendazim + 5.0% iodopropynyl butylcarbamate (IPBC); aqueous dispersion (comparison dispersion)

VI) 4.38% 2-methylthio-tert-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051) + 10.0% carbendazim + 10.0% iodopropynyl butylcarbamate (IPBC);

aqueous dispersion (comparison dispersion)

VII) 4.38% 2-methylthio-tert-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051) + 10.0% carbendazim + 5.0% zinc pyrithione; aqueous dispersion

VIII) 4.38% 2-methylthio-tert-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051) + 10.0% carbendazim + 10.0% zinc pyrithione; aqueous dispersion

IX) 5% carbendazim, 7.8% 2-thiocyanomethylthiobenzothiazole and 1.8% 2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine; aqueous dispersion (comparison dispersion)

Procedure

In separate batches, 0.25%, 0.5%, 1.0% and 2.0%, respectively, of test substance were incorporated into the masonry paint, and the fungicidal or algistatic properties were determined by the test methods indicated.

Results:

Algistatic properties: without stress due to leaching

	Use concentration	Inhibitory zone in mm	Surface growth	Discoloration
Blank value		0	+ +	none
I)	2.0 % 1.0 % 0.5 % 0.25 %	>18 >18 >18 >18	- - + +	somewhat more yellowish somewhat more yellowish none none
II)	2.0 % 1.0 % 0.5 % 0.25 %	>18 >18 12 7	- - - +	none none none none
III)	2.0 % 1.0 % 0.5 %	>18 10 5	+ +* +*	some degree of yellow discoloration minimal yellow discoloration none
IV)	2.0 % 1.0 % 0.5 %	>18 10 0	+ +* +*	severe yellow discoloration minimal yellow discoloration none
V)	2.0 % 1.0 % 0.5 %	>18 >18 5	- + +	slight yellow discoloration some degree of yellow discoloration none
VI)	2.0 % 1.0 % 0.5 %	>18 >18 15	+ + +*	severe yellow discoloration slight yellow discoloration some degree of yellow discoloration
VII)	2.0 % 1.0 % 0.5 %	>18 11 0	+ -* +*	none none none
VIII)	2.0 % 1.0 % 0.5 %	>18 13 0	- -* -	none none none
IX)	2.0 % 1.0 % 0.5 %	5 0 0	+* + +	markedly more yellow than reference somewhat more yellow than reference none

Algistatic properties: stress due to 72 hours leaching

	Use concentration	Inhibitory zone in mm	Surface growth	Discoloration
Blank value		0	+ +	none
I)	2.0 % 1.0 % 0.5 % 0.25 %	>18 0 0 0	- -* + +	none none none none
II)	2.0 % 1.0 % 0.5 % 0.25 %	0 10 10 0	- -* - +	none none none none
III)	2.0 % 1.0 % 0.5 %	>18 12 5	+ +* +*	none none none
IV)	2.0 % 1.0 % 0.5 % 0.25 %	11 11 0	+* +* +*	none none none
V)	2.0 % 1.0 % 0.5 %	0 0 0	+* +* +*	none none none
VI)	2.0 % 1.0 % 0.5 %	10 0 0	+* +* +*	none none none
VII)	2.0 % 1.0 % 0.5 %	>18 12 0	+ +* +*	none none none
VIII)	2.0 % 1.0 % 0.5 %	>18 0 0	- +* +*	none none none
IX)	2.0 % 1.0 % 0.5 %	0 0 0	+* + +	yellow discoloration very slightly more yellow than reference none

* = poor growth

Key: - = no growth

\+ = some degree of growth

++ = moderate growth

+++ = copious growth

Fungicidal properties: without stress due to leaching

	Use concentration	Test micro-organisms AN		PF		AL	
		1st	2nd	1st	2nd	1st	2nd
Blank value		5	5	5	5	5	5
I)	2.0 % **	0	0	0	0	0	2
	1.0 % **	0	(0)	0	0	1	2
	0.5 %	(0)	1	0	0	2	3
	0.25 %	1	1	0	0	3	4
II)	2.0 %	0	0	0	0	0	2
	1.0 %	(0)	(0)	0	0	1	3
	0.5 %	1	1	0	0	2	3
	0.25 %	1	1	0	0	3	4
III)	2.0 %**	0	0	0	0	1	3
	1.0 %**	(0)	(0)	0	0	5	5
	0.5 %	(0)	(0)	0	0	5	5
IV)	2.0 %**	0	0	0	0	1	1
	1.0 %**	0	0	0	0	1	3
	0.5 %	(0)	1	0	0	5	5
	0.25 %						
V)	2.0 %**	0	0	0	0	0	(0)
	1.0 %**	0	0	0	0	0	(0)
	0.5 %	(0)	(0)	0	0	2	3
VI)	2.0 %**	0	0	00	00	0	0
	1.0 %**	0	0	0	0	0	(0)
	0.5 %**	0	0	0	0	2	2
VII)	2.0 %	0	0	0	0	0	0
	1.0 %	(0)	(0)	0	0	0	2
	0.5 %	(0)	(0)	0	0	5	5
VIII)	2.0 %	0	0	0	0	0	0
	1.0 %	0	(0)	0	0	0	0
	0.5 %	(0)	(0)	0	0	0	1
IX)	2.0 %**	(0)	1	0	0	1	1
	1.0 %**	(0)	1	0	0	1	1
	0.5 %	1	1	0	0	2	3

** = (somewhat or much) more yellowish than reference, discoloration relative to reference

Fungicidal properties: stress due to 72 hours leaching

	Use concentration	Test micro-organisms AN		PF		AL	
		1st	2nd	1st	2nd	1st	2nd
Blank value		5	5	5	5	5	5
I)	2.0 %	(0)	1	0	0	5	5
	1.0 %	1	1	0	0	5	5
	0.5 %	1	1	0	0	5	5
	0.25 %	2	2	0	0	5	5
II)	2.0 %	1	1	0	0	5	5
	1.0 %	2	2	0	0	5	5
	0.5 %	2	2	0	0	5	5
	0.25 %	2	2	0	0	5	5
III)	2.0 %	(0)	(0)	0	0	5	5
	1.0 %	(0)	(0)	0	0	5	5
	0.5 %	(0)	1	0	0	5	5
IV)	2.0 %	(0)	(0)	0	0	1	3
	1.0 %	(0)	1	0	0	3	4
	0.5 %	1	1	0	0	5	5
	0.25 %						
V)	2.0 %	(0)	(0)	0	0	5	5
	1.0 %	1	1	0	0	5	5
	0.5 %	2	2	0	0	5	5
VI)	2.0 %	(0)	(0)	0	0	2	3
	1.0 %	(0)	1	0	0	4	5
	0.5 %	1	1	0	0	5	5
VII)	2.0 %	(0)	(0)	0	0	(0)	2
	1.0 %	(0)	1	0	0	2	4
	0.5 %	2	2	0	0	5	5
VIII)	2.0 %	(0)	(0)	0	0	0	1
	1.0 %	(0)	1	0	0	(0)	2
	0.5 %	1	2	0	0	2	3
IX)	2.0 %	(0)	1	0	0	1	2
	1.0 %	1	1	0	0	2	3
	0.5 %	2	2	0	0	3	5

Key: 00 = entire plate free from growth
0 = zone formation (no growth around the sample)
(0) = fungal growth up to the sample
1 = only sample edge covered with growth
2 = sample covered with growth from the edge inwards (less than 25 %)
3 = sample surface shows growth of individual colonies (25 % to 75 %)

4 = sample surface covered with extensive growth (75 % and more, but not the entire area)

5 = sample surface totally covered with growth (100 %)

Assessment: The Acticid copy I), with and without stress due to leaching, is slightly more effective against algae than II), which contains 7% of Kathon 893. At a use concentration of 2% and 1% and without stress due to leaching, the Acticid EP copy I) results in some degree of yellowing of the test material.

The Acticid EP copy I) has a slightly better fungidical activity than II) (without and with stress due to leaching, see AN and AL results). With stress due to leaching, both products have no activity against Alternaria alternata.

Assessment of dispersions III), IV), which contain Amical 48, and V), VI), which contain IPBC, and VII), VIII) which contain zinc pyrithione, relative to each other and in comparison with IX):

Rank (1 better than 2 better than 3) regarding

	Carbendazim + Irgarol 1051 +		
	Amical 48 or	IPBC or	Zinc pyrithione
Discoloration of the test material	3	2	1
Resistance to leaching (AL)	2	3	1
Activity against AL	3	1(2)	2(1)
Activity against AN	2	1	2
Activity against PF	2	1	2
Activity against algae without stress due to leaching:			
Surface growth	3	2	1
Formation of inhibitory zones	2	1	2

Activity against algae with stress due to leaching:			
Surface growth	1	2	1
Formation of inhibitory zones	2	2	1

Discoloration:

III) and IV), which contain Amical 48 -> discoloration with high use concentrations

V) and VI), which contain IPBC -> discoloration with high use concentrations

VII) and VIII), which contain zinc pyrithione -> no discolorationnot even at high use concentrations

Rank of activity against AL:
zinc pyrithione > IPBC >> Amical 48.

As regards the activity against Alternaria, VII) and VIII), which contain zinc pyrithione, and V) and VI), which contain IPBC, perform equally well as IX). (II) and IV), which contain Amical 48, do not perform as well as IX)). With regard to the activity against AN and PF, all 3 active ingredients even outperform IX).

The resistance to leaching (assessed with regard to activity against Alternaria after stress due to leaching) is most pronounced in the case of VII) and VIII), which contain zinc pyrithione. After stress due to leaching, there still exists activity against Alternaria in the presence of zinc pyrithione VII) and VIII) (in contrast to V) and VI), which contain IPBC and III) and IV), which contain Amical 48), this activity against Alternaria is in the same order of magnitude as the activity of IX).

In all 3 preparations, the algistatic activity with and without stress due to leaching is good or satisfactory and better than that of IX).

At 2% and 1% of IX), some degree of yellowish discoloration of the test material which had such properties imparted to it was observed, even after stress due to leaching.

Similar results are also obtained with preservatives which contain a dispersant/solubilizer/thickener system composed of 0.5% by weight of Rhodopol 50 MD + 0.2% by weight of Lutensol TO 5.

Film preservative with compounds from active ingredient classes a) and b)

The combinations tested contained in each case 5% 2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine (Irgarol 1051) and

- 8.7% diiodomethyl-p-tolyl sulphone (Amical 48) or
- 7.6% iodopropynyl butylcarbamate (IPBC)
- 10.0% zinc pyrithione

X): 5% Irgarol 1051 + 8.7% Amical 48;
aqueous dispersion; thickener system: Rhodopol 50 MD + Lutensol TO 5; wet superfine grinding of the active ingredients; homogeneous whitish/yellowish dispersion, low-odour

XI: 5% Irgarol 1051 + 6.7% IPBC;
aqueous dispersion; thickener system: Rhodopol 50 MD + Lutensol TO 5; wet superfine grinding of the active ingredients; homogeneous whitish dispersion, low-odour

XII: 5% Irgarol 1051 + 10% zinc pyrithione;

aqueous dispersion; thickener system: Rhodopol 50 MD + Lutensol TO 5; wet superfine grinding of the active ingredients; homogeneous whitish dispersion, low-odour

Testing preparations based on 2-methylthio-4-tert-butylamino-6-cylcopropylamino-s-triazine (Irgarol 1051) + diiodomethyl p-tolyl sulphone (Amical 48) or iodopropynyl butylcarbamate (IPBC) or zinc pyrithione for fungicidal/algicidal activity

Test material:	100% acrylic masonry paint (see above)	
Test type:	Imparting fungicidal properties Imparting algistatic properties	
Test microorganisms, algae:	Chlorella fusca	CF
Test microorganisms, fungi:	Aspergillus niger	AN
	Penicillium funiculosum	PF
	Alternaria alternata	AL

Test substances:

Blank value Masonry paint, unpreserved

Composition:

X) 5% Irgarol + 8.7% Amical 48 - aqueous dispersion

XI) 5% Irgarol + 6.7% IPBC - aqueous dispersion

XII) 5% Irgarol + 10% zinc pyrithione - aqueous dispersion

Procedure

In separate batches, 0.5%, 1.0% and 2.0%, respectively, of test substance were incorporated into the masonry paint, and the fungicidal or algistatic properties were determined by the test methods indicated.

Results:

Algistatic properties: without stress due to leaching

	Use concentration	Inhibitory zone in mm	Surface growth	Discoloration
Blank value		0	+ +	none
X)	2.0 %	>18	-	markedly more yellow than
	1.0 %	>18	-	reference more yellow than
	0.5 %	>18	-	reference no discoloration
XI)	2.0 %	>18	-	severe yellow discoloration
	1.0 %	>18	-	more yellow than reference
	0.5 %	>18	-	no discoloration
XII)	2.0 %	>18	-	no discoloration
	1.0 %	>18	-	no discoloration
	0.5 %	>18	-	no discoloration

Algistatic properties: stress due to 72 hours leaching

	Use concentration	Inhibitory zone in mm	Surface growth	Discoloration
Blank value		0	+ +	none
X)	2.0 %	>18	-	no discoloration
	1.0 %	>18	-	no discoloration
	0.5 %	0	+*	no discoloration
XI)	2.0 %	>18	-	no discoloration
	1.0 %	11	-	no discoloration
	0.5 %	5	-	no discoloration
XII)	2.0 %	>18	-	no discoloration
	1.0 %	>18	-	no discoloration
	0.5 %	14	-	no discoloration

* = poor growth

Key: - = no growth

\+ = some degree of growth

++ = moderate growth

+++ = copious growth

Fungicidal properties: without stress due to leaching

	Use concentration	Test microorganisms AN		PF		AL	
		1st	2nd	1st	2nd	1st	2nd
Blank value		5	5	5	5	5	5
X)	2.0 %	0	0	(0)	(0)	1	1
	1.0 %	1	1	(0)	(0)	1	3
	0.5 %	1	1	2	3	4	5
XI)	2.0 %	0	0	0	0	0	0
	1.0 %	0	0	0	0	0	(0)
	0.5 %	(0)	1	(0)	(0)	(0)	1
XII)	2.0 %	0	2	0	0	0	0
	1.0 %	(0)	2	0	0	0	0
	0.5 %	1	3	0	(0)	0	1

Fungicidal properties: stress due to 72 hours leaching

	Use concentration	Test microorganisms AN		PF		AL	
		1st	2nd	1st	2nd	1st	2nd
Blank value		5	5	5	5	5	5
X)	2.0 %	(0)	1	1	1	1	3
	1.0 %	1	1	1	1	4	5
	0.5 %	1	2	5	5	5	5
XI)	2.0 %	(0)	2	(0)	1	1	3
	1.0 %	2	3	2	3	3	4
	0.5 %	4	5	2	3	5	5
XII)	2.0 %	(0)	1	0	1	0	1
	1.0 %	3	4	0	1	0	2
	0.5 %	5	5	1	4	2	4

Key: 00 = entire plate free from growth
0 = zone formation (no growth around the sample)
(0) = fungal growth up to the sample
1 = only sample edge covered with growth
2 = sample covered with growth from the edge inwards (less than 25 %)
3 = sample surface shows growth of individual colonies (25 % to 75 %)
4 = sample surface covered with extensive growth (75 % and more, but not the entire area)

5 = sample surface totally covered with growth (100 %)

Assessment	Activity			
Product	AN without	AN with	PF without	PF with
X)	(+)	(+)	(+)	(-)
XI)	+	(-)	+	(+)
XII)	(+)	(-)	+	(+)

Assessment	Activity			
Product	AL without	AL with	CF without	CF with
X)	(-)	(-)	+	(+)
XI)	+	(-)	+	+
XII)	+	(+)	+	+

Discoloration
(-)
-
+

Key:
AN = Aspergillus niger PF = Penicillium funiculosum
AL = Alternaria alternata CF = Chlorella fusca
without/with = without/with stress due to leaching
\+ good/acceptable
(+) just about acceptable
(-) good/acceptable within limitations
\- insufficient/not acceptable

Results

Discoloration:

X) Aqueous dispersion based on 5 % Irgarol + 8.7 % Amical: At use concentrations of 1% and 2%, a standard masonry paint discolours to somewhat more yellow and

markedly more yellow, respectively, than the blank value.

XI) Aqueous dispersion based on 5 % Irgarol + 6.7 % IPBC:
At use concentrations of 1% and 2%, a standard masonry paint discolours to more yellow and much more yellow, respectively, than the blank value.

XII) Aqueous dispersion based on 5 % Irgarol + 10.0 % zinc pyrithione:
At a use concentration of 2%, a standard masonry paint does not discolour.

- Fungicidal activity:

X) exhibits only just good activity, or an activity within limitations, against fungi. Marked failure to act is evident in the case of PF and AL.

XI) shows a good (without stress due to leaching) or only just good activity within limitations (with stress due to leaching) against fungi. In total, the spectrum of action against the fungi tested is relatively balanced.

XII) has a good to only just good activity (without stress due to leaching), or only just good activity to activity within limitations (with stress due to leaching), against fungi.

- Algicidal activity:

The algicidal activity of the preparations X) to XII) is good. With stress due to leaching, X) performs less well than XI) and XII).

CLAIMS

1. Preservative, characterized in that it comprises
a) at least one compound from the class of the pyrithiones which are active against Alternaria and
b) at least one compound from the class of the algicidally active triazines and/or
c) at least one compound from the classes of the fungicidally active benzimidazoles or thiophenes
and customary auxiliaries,
where, in the absence of benzimidazole or thiophene, an additional presence of algicidal urea compounds or biocidal hydrolysable polymeric resins is excluded.

2. Preservative according to Claim 1, characterized in that the total active ingredient content is in a range from 1 to 99% by weight, preferably 2 to 90% by weight, and in particular 5 to 80% by weight, and the remainder is composed of customary formulation auxiliaries.

3. Preservative according to Claim 1 or 2, characterized in that it comprises
a) 1.0 - 45.0% by weight of pyrithione compound and
b) 1.0 - 35.0% by weight of triazine compound and/or
c) 1.0 - 45.0% by weight of benzimidazole or thiophene compound

4. Preservative according to Claim 3, characterized in that it comprises
a) 2.0 - 25.0% by weight of pyrithione compound and
b) 2.0 - 15.0% by weight of triazine compound and/or
c) 2.0 - 25.0% by weight of benzimidazole or thiophene compound

5. Preservative according to Claim 4, characterized in that it comprises
a) 2.0 - 15.0% by weight of pyrithione compound and
b) 2.0 - 10.0% by weight of triazine compound and/or
c) 2.0 - 15.0% by weight of benzimidazole or thiophene compound

6. Preservative according to any one of the preceding claims, characterized in that the pyrithione compound is zinc pyrithione, the triazine compound is 2-methylthio-4-t-butylamino-5-cyclopropylamino-s-triazine, N^2,N^4-diiso-propyl-6-methylthio-1,3,5-triazine-2,4-diamine or N^2-tert-butyl-N^4-ethyl-6-methylthio-1,3,5-triazine-2,4-diamine, the benzimidazole compound is carbendazim and/or the thiophene compound is N-cyclohexyl-2-aminobenzothiophene S,S-dioxide.

7. Preservative according to any one of Claims 1 to 6, characterized in that it comprises 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, carbendazim and zinc pyrithione.

8. Preservative according to any one of Claims 1 to 6, characterized in that it comprises 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine and zinc pyrithione.

9. Preservative according to any one of Claims 1 to 6, characterized in that it comprises carbendazim and zinc pyrithione.

10. Preservative according to any one of the preceding claims, characterized in that it comprises one or more further algicidal and/or fungicidal active ingredients.

11. Preservative according to Claim 10, characterized in that the further active ingredients are halogen-free.

12. Preservative according to any one of the preceding claims, characterized in that the customary auxiliaries comprise dispersants, high-boiling solubilizers, anti-caking agents, thickeners, low-temperature stabilizers, fillers and/or carriers.

13. Preservative according to any one of the preceding claims, characterized in that the dispersants comprise fatty alcohol ethoxylates and/or salts of polyacrylic acid.

14. Preservative according to any one of the preceding claims, characterized in that the high-boiling solubilizers comprise glycols, their esters or their ethers.

15. Preservative according to any one of the preceding claims, characterized in that the preservative components have a particle size of in each case less than 70 µm, preferably less than 30 µm and in particular less than 10 µm.

16. Preservative according to any one of the preceding claims, characterized in that the combination of active ingredients is in the form of a powder, a solution, a dispersion or a paste.

17. Process for the preparation of a preservative according to any one of Claims 1 to 16, characterized in that the constituents are mixed with each other, solid active ingredient components being subjected to superfine grinding in the presence of the remaining formulation auxiliaries in water to give a premix and the liquid active ingredient components subsequently being stirred.

18. Use of a preservative according to any one of Claims 1 to 16, for imparting fungicidal and algistatic properties to paints, varnishes and renders, or in textile finishing, sealants, glues and adhesives.

INTERNATIONAL SEARCH REPORT

Inter .onal application No.
PCT/IB 98/00099

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: A01N 43/40, A01N 43/70, A01N 47/18, A01N 43/12, C09D 5/14, C09D 5/16
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: A01N, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Patent Abstracts of Japan, Vol 7,No 143, C-172 abstract of JP 58-57367 A (Shintou Toriyou K.K.), 5 April 1983 (05.04.83) --	1-18
X	GB 2274779 A (YUKONG LIMITED), 10 August 1994 (10.08.94), the claims (formula IV); the examples --	1-18
X	WO 9506091 A1 (BAYER AKTIENGESELLSCHAFT), 2 March 1995 (02.03.95), page 6, line 23; page 17; page 5, line 12, the claims --	1-18

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 March 1998	23.04.98
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer GERD STRANDELL

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB 98/00099

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Patent Abstracts of Japan, Vol 12,No 479, C-552 abstract of JP 63-196502 A (Shinto Paint Co Ltd), 15 August 1988 (15.08.88)	1-18
X	Patent Abstracts of Japan, Vol 12,No 482, C-553 abstract of JP 63-196657 A (Sumitomo Chem Co Ltd), 15 August 1988 (15.08.88)	1-18
X	Patent Abstracts of Japan, Vol 18,No 601, C-1274 abstract of JP 6-227912 A (Sekisui Chem Co Ltd), 16 August 1994 (16.08.94)	1-18
A	EP 0513409 A1 (RIEDEL-DE HAEN AKTIENGESELLSCHAFT), 19 November 1992 (19.11.92), the claims; the examples	1-18
A	EP 0003749 A1 (CIBA-GEIGY AG), 5 Sept 1979 (05.09.79)	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/03/98

International application No.
PCT/IB 98/00099

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